BODIES CONTAINING HIGH QUANTITIES OF FLY ASH OR COAL MINING WASTE

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SUMMARY

Bodies containing high quantities of fly ash and coal mining waste can be shaped by employing various shaping technologies. The main technological literature on the subject of ceramics primarily describes shaping by means of extrusion and dry pressing.
However, the soft-mud method can also be used to manufacture building bricks with as much as 90% fly ash. The investigation described here has shown that bodies containing up to 85% fly ash can be adequately processed and shaped when using Dutch fly ash and (extremely) plastic Dutch clays. The clays applied were, by Dutch standards, on the plastic side (specific surface 120 – 160 m^2/g, measured with water adsorption). Such a plastic clay is necessary to compensate for the strong decrease in workability (plasticity) of bodies containing a high quantity of fly ash or coal mining waste.

Bodies containing up to 75% coal mining waste can also be adequately homogenised and shaped. Ground coal mining waste has more bonding and plasticising properties owing to its relatively high carbon content. For mixtures incorporating coal mining waste, less plastic clays can be used. In that case, loamy sandy clays would probably also be suitable for use as ceramic binders and plasticisers.

The bodies with the highest fly ash or coal mining waste content were generally the easiest to process. The filling of the moulds, pressing and removal of the product from the mould was 'good' to 'problem-free'. The highly 'plastic' character of the clays from Munnikenland and, to a lesser extent, the clays from Woerden was compensated by the decreasing effect of the fly ash and the rather coarsely ground coal mining waste.

The experiments were not oriented towards total optimisation of the entire process, up to and including the firing process. One of the mixtures, clay from Woerden plus coal mining waste, later proved to have been insufficiently fired.

Mixtures with bentonite display rather extreme processing properties and, if used on a large scale, are almost certainly unsuitable as binders and plasticisers. In addition, they are expensive in comparison with other materials.

1 INTRODUCTION

Discussions of the positive and negative qualities of products manufactured through various ceramic processes, using bodies containing high quantities of such residues as carbon bearing coal mining waste or fly ash have been appearing in the specialist literature with growing regularity. In most cases, these were small-scale laboratory experiments, though

experience with large-scale practical experiments do appear from time to time. Further, in the past, the majority of practical experiences as well as small-scale laboratory experiments with a high body quota of residues involved extruded or dry-pressed bodies (see: Bibliography). The soft-mud method is highlighted in the experiment described here. Although a regularly implemented shaping method in the Netherlands, it is rarely used elsewhere in the world. This experiment investigated whether or not bodies containing high quantities of fly ash and/or coal mining waste could be shaped using soft-mud moulding, as well as whether the product qualities of the resulting building ceramics met the standards after drying and firing.

As this experiment involved a relatively circumscribed, focused investigation, a number of limiting factors had to be considered in its design. The intention was to explicitly determine the upper limit of residue (such as fly ash and carbon bearing coal mining waste) content in a clay-based body, three different bodies of clay were used in the experiment.
Although it is known that a ceramic product's properties are not only determined by the body's composition (the recipe), but also its preparation, shaping method (with plastic shaping: water content and/or plasticity), drying method and firing curve (temperature, time), these separate phases of the ceramics process are generally not optimised.
The possible positive energy effect of carbon residues in fly ash and coal mining waste during the ceramic firing process was not considered in this experiment.
A large number of process parameters were maintained constant to allow mutual comparison of the wide range of recipes investigated and the resulting products.

2 LITERATURE REVIEW

2.1 bodies with fly ash

Using fly ash or coal mining waste as a raw material or additive to building ceramics as bricks or roofing tiles is frequently described in the literature. Although the share of electricity produced by coal-fired generating stations in the Netherlands is meagre, there have been all manner of investigations by Dutch organisations such as TNO and TCKI into the possibilities of processing the fly ash from these power generating stations into such products as bricks and roofing tiles. Low concentrations (up to 25% by weight) have been commonly added to generally more plastic clays to lower the plasticity of the bodies that are often difficult to process. Bodies containing higher concentrations up to 70%, even 85% of fly ash, however, can be formed, fired and used.
The general conclusion was commonly: "Yes, it is possible, but..."
Problems are expected as regards leaching, formation of undesired surface discoloration, increased radiation load with some ashes and, late-stage environmental impact during demolition.

Possible adverse effects including radiation load apply particularly to bottom ashes. Investigations into fly ashes have demonstrated, however, that this material is harmless in that respect.
The then state of affairs as regards the use of fly ash was jointly investigated by ECN, KEMA, KNB and MT-TNO Apeldoorn and collated in a literature study [1]. This study

incorporated 65 references. The most common conclusions pointed out the environmental-hygienic consequences of adding fly ash to building ceramics.
A somewhat older, though extremely comprehensive investigation [4] into the production of dry-pressed and stiff-extruded fly ash bricks took place in England. The body preparation and shaping occurred without any significant problems. The bricks revealed a remarkable "post-stiffening" effect owing to the relatively short humidification time prior to shaping through which the possibility to handle the shaped brick was improved dramatically. The drying time of these – for the most part dry – products was rather short. The bodies that were allowed to soak for 24 hours prior to extrusion were much more sensitive to dryness. In England, experiments were also conducted that described bodies based on a patent from Corson in which the recipes used and the products manufactured were composed of >85% fly ash and bed ash together with 1 – 2% bentonite. Nearly all the bricks produced containing >75% fly ash have properties qualified as 'reasonable' to 'good', and remain in a good state after 7 years of testing under weather and climate proof conditions.

An exhaustive study of the various scenarios to manage the fly ash problem in Europe and in developing countries was presented in the 'Proceedings of the International Conference on Fly Ash Disposal and Utilisation', January 1998, New Delhi, India [5]. The recycling of these residues in developing countries remains at comparatively low levels or is even minimal in extent. This is the result of several fundamental challenges, primarily economic, but also geographic and logistic (fly ash production sites and possible users are situated too far from one another), market technology, research facilities, etc. Similar justifications are still put forward in Europe to explain why residues are still not recycled to the full 100%.
It has been established that there is an enormous gulf between the demand and supply of construction materials in India (and most likely in other developing countries as well), in spite of which the fly ash industry, which could meet the demand for building materials, is still not thriving.
Reasons for this include:

- competition with the age-old and widely accepted ceramic brick;
- low acceptance of residue-based products;
- high costs of technology transfer and capital investments;
- lack of good shaping equipment (presses);
- lack of investors and/or entrepreneurs in the field of construction materials.

Examination of a large-scale practical trial was presented in one of the publications, in which mixtures of local clay were combined with ash from a local power station in a fly ash to clay ratio of 60:40. This was done following an earlier feasibility study at a regional research institute. The local brick maker manufactured 14,600,000 bricks over 6 years, all of which were sold within the local market. Because the ash was supplied for 'free' as a raw material, the production costs could be minimised. Eventually, the result was a cheaper brick that appeared to be economically viable for the population groups with even the lowest incomes.
In the May – June 1998 issue of the journal 'L'industria dei laterizi', M. Dondi published an extensive overview article including a comparison of all the agricultural, small-scale and large-scale industrial waste as well as an investigation into their use as a secondary basic ingredient for the production of bricks.
The dry press method as a shaping process is assumed in the majority of the investigations, such as those described in the 100 references, in addition extrusion processes are widely used. The soft-mud method is applied as a manufacturing process in only a minority of the experiments. Because the experiments are widely divergent in terms of the nature of the fly

ash used, the type of binding clay, and the presence (or absence) of additional plasticisers, the results of the experiments cannot be compared or only compared to an extremely limited degree.
This publication shows that it is possible to shape bodies containing 60 – 75% fly ash.

2.2 Bodies with coal mining waste

The number of publications covering the use of coal mining waste as a secondary basic ingredient in the brick making industry is markedly smaller compared to similar publications involving fly ash. The most common reason for the use of this waste stream is the high content of residual carbon in the body. Energy savings during the firing of the shaped brick including coal mining waste of 40%, with peaks reaching 60%, have been described. In theory, coal mining waste contains the same elements, meaning the same chemical composition as the habitually used clays, particularly silicon oxide, aluminium oxide, iron oxide, and to a lesser extent sodium and potassium oxides.
The amount of coal mining waste used varies around an average of 10 – 15% in the body, to practically 100%. In this last case, the coal mining waste is used as a complete alternative for clay, as a bulk raw material.
The technological qualities vary widely, from plasticised to plastic-reducing. Granule size distribution and other qualities of the base clay with respect to the coal mining waste added has a deterministic effect. A porous end product generally results from firing a product containing coal mining waste.
Drying and firing shrinkage are influenced through the addition of coal mining waste. Drying shrinkage is generally reduced and the entire drying process runs more smoothly. Firing shrinkage is primarily affected by the chemical composition, the amount of flux in the coal mining waste, and the firing temperature. The biggest challenge rests in the length of the necessary firing time as the high content of combustible carbon requires a modified firing process.
The onset of black core formation already appears in the laboratory experiments described below.
The use of coal mining waste (and other mining-related waste, including that gained by washing mining products) both mixed in clays, and used as a bulk material for building ceramics, generally offers positive results from a technological and from an economic standpoint. The firing process must, however, be adjusted to the high content of organic material and the bodies must be relatively lean: clays that are too plastic should not be used as binders.

3 RESEARCH DESIGN AND PROTOCOL

3.1 Basic materials

Two normal but plastic Dutch clays, a bentonite, a type of fly ash and a coal mining waste were selected as raw materials.
The most important data regarding the two clays and the bentonite are presented below:

<u>clays, binders for the residues:</u>

- Roofing tile clay from Woerden — fraction < 2 μm: 38.0 %
  specific surface (water absorption) 119 m^2/g

- Roofing tile clay from Munnikenland fraction < 2 µm: 49.5 %
  specific surface (water absorption) 160 m^2/g

- Bentonite, Colclay A90 85 % Montmorillonite
  water absorption (Enslin, 24 hour) 100 %

The following residues were processed at TNO.

- Coal mining waste, from the stocks of coal waste from the mines in Limburg (NL).

Supplied by Nievelsteen BV.
Slate with a residual carbon content of approximately 10% (L.O.I.) and a specific surface of 64 m^2/g, measured using the water absorption method.

- Fly ash
  Product from a normal coal-fired generating station (supplied by Vliegas Unie, in Nijmegen (NL)).

The two clays and the bentonite were dry grounded to a powder.
The fly ash available was also a dry powder.
The coal mining waste ranged from a rough powder to chunks (several cm in size) and ground prior to the experiment in a hammer mill and sorted using a 4-mm sieve.
The dry, ground clays and residues were mixed in various proportions, using a Hobart mixer, with water, into a relatively workable mass and allowed to soak for at least 24 hours.
After adding extra water, the bodies are homogenised and brought to a plasticity of 6 mm Pfefferkorn residue level and shaped.
Shaping took place using a De Boer laboratory press, which maintained pressure of 50 – 70 bars in the cylinders. The laboratory samples could be rapidly reproduced with this small-scale industrial brick shaping machine with the following dimensions 100 x 50 x 25 cm, which is 1/8th the standard Waal format. 15 trial bricks were made per recipe composition.

photo 1: The laboratory version of the shaping press, manufactured by De Boer.

The bricks were carefully allowed to dry for 96 hours under controlled conditions. The samples were then fired in a gas-burning oven with the following curve:
temperatures of 1,030 C achieved over approximately 25 hours, maintained for an hour and then cooled over 25 hours to room temperature.
Although the bricks were fired at the same time, regardless of their varying compositions and different types of clay, in a single oven and using the same firing curve, large differences in product quality were unavoidable: several samples were fired at a to high temperature, while other were insufficiently fired.

photos 2, 3 and 4: The bricks produced.

photo 2: See caption on the rear of the photo.
photo 3: See caption on the rear of the photo.
photo 4: See caption on the rear of the photo.

3.3 Evaluating and testing the trial bricks

During the entire process, the behaviour of the bodies was recorded during preparation, shaping, drying and firing. Furthermore, the various intermediary stages were characterised.

The following properties were established:

- visual evaluation of the mixing process.
- nature (workability, consistency) and homogeneity of the mixtures.
- visual evaluation prior to and during pressing
  - loading the press;
  - pressing;
  - removing surplus clay;
  - removing from the mould.
- visual evaluation of the bricks following pressing.
- measurements of the bricks following drying
  - drying shrinkage (compared to the wet measurements);
  - dry weight and measurements, calculating the apparent density;
  - post-drying flexibility strength using 5 trial bricks;
  - visual evaluation of the entire brick after breaking, and of the plane of fracture.
- measurements of the bricks after firing (at one single temperature)
  - firing shrinkage (compared to the dry measurements);
  - measurements and weight following firing, calculating the apparent density;
  - spontaneous water absorption;
  - post-firing flexibility strength using 5 trial bricks;
  - visual evaluation of the entire brick after breaking, and of the plane of fracture.

The results of the evaluation and the characterisation of the dry and fired product are presented below.

The Technisch Centrum voor de Keramische Industrie (TCKI) in De Steeg, the Netherlands, a technical centre for the ceramics industry, is currently conducting upscaling trials, based on the previously described bodies that produced quality products on a small laboratory scale to manufacture Waal-format bricks. Upscaling the laboratory experiments ($1/8^{th}$ scale) to a 1:1 technical testing does not happen automatically or without problems. The quadrate increases with upscaling, as does the content of the brick by a factor of 3. Drying, firing, and the technological qualities are consequently difficult to predict, which explains the supplementary research by TCKI.

4 RESULTS

The results from the evaluation can be summarised in the following table:

table 1 -
Properties of fly ash and coal mining waste bearing bodies during working, shaping and firing, and a few characteristics of the fired product. (laboratory samples, $1/8^{th}$ scale)
MM = Clay from Munnikkenland / Coal Mining Waste
WM = Clay from Woerden / Coal Mining Waste
MV = Clay from Munnikkenland / Fly Ash

WV = Clay from Woerden/ Fly Ash
BM = Bentonite / Coal Mining Waste
BV = Bentonite / Fly Ash
35, 50, 75 = body percentage of Coal Mining Waste in the mix
50, 75, 85 = body percentage of Fly Ash in the mix
90 resp. 88 = body percentage of Coal Mining Waste compared to Fly Ash in the bentonite mixture

In table 2 below, the results of the characterisations (the average of the observations) of the dried and fired laboratory samples are presented.

Table 2 -
Overview of the average of the results following the characterisation of the dried and fired laboratory bricks (1/8th laboratory scale) with coal mining waste and fly ash.
See table 1 for the body codes.

Indicated below, the measurement results of the mixtures of the clay from Woerden (W) with fly ash (V) and coal mining waste (M) are presented graphically.
Note: The various qualities, such as the post-firing strength and the firing behaviour in general as regards the investigation described here are <u>not</u> optimised.

figure 1 -
graphic representation of the measurement results of a few clays, unmixed and after mixing the clay with high percentages of fly ash and coal mining waste.
See table 1 for the body codes.
W0 is the clay from Woerden without additives.

5 CONCLUSIONS

The experiences with coal mining waste and fly ash bearing clay bodies can be summarised as follows:

1. The bodies containing a great deal of **fly ash or coal mining waste**, 50, 75 and 85% by weight, can be shaped by means of the soft-mud method.
   If extremely plastic clays and bentonite are used to bind the fly ash and/or make it workable and mouldable, problems can occur with regard to the highest content of that clay and/or the lowest percentage of fly ash.
   Here, fly ash acts as an effective opening agent, especially with higher percentages. In general, clay bodies with **the highest concentrations** of fly ash or coal mining waste were the easiest to work. Filling the moulds, pressing and removing the product from the mould was 'good' to 'problem-free'.

2. **Problems can be expected**, most certainly in the case of experiments on a larger scale or in a later practical industrial situation, **when homogenising** the bodies. Both the fly ash and the coal mining waste must be thoroughly mixed and homogenised with the binding clay.

As to the preparation of the bodies, it will be necessary to establish a plan such as is present at traditional extrusion-process manufacturers.

3. A few of the small bricks with a large amount of coal mining waste showed **the onset of black cores** after firing. This means that the **firing regime** must be adapted and/or allowed to occur more slowly for firing in practical industrial situations.

4. The **drying and firing experiments** did not produce any surprising results. The results and the appearance of the product after drying and firing are mainly determined by the plasticity of the clays used. The chemical disposition and the mineralogy control the firing behaviour; the extent of firing and firing shrinkage.

5. **Bentonite** does not qualify as a binder for fly ash and coal mining waste owing to the laborious working qualities, extreme moisture content with shaping, and the drying and firing behaviour.

6. Although this does not form part of the investigation described here, the following **specific advantages of the soft-mud method** compared with extrusion can be mentioned on the basis of personal experience and a general knowledge of the literature:
   - Soft-mud bricks are more frost-resistant than bricks manufactured using the extrusion process, owing to the more homogenous brick structure which has not been subject to any .
   - The soft-mud method as a shaping process is, in terms of the flexibility in body composition (mineralogical, chemical, morphological) and variations in moisture content, more attractive than manufacturing using the extrusion process.
   - The shaping energy required is for the most part lower than that needed for extrusion, although in the investigation described here, where 'difficult to process' residues had to form a homogenous mix with the clay, more needs to be done to homogenise the body than is usually the case in the normal Dutch situation with a soft-mud press.

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